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Yields of Glyoxal and Methylglyoxal from the NOx-Air Photooxidations of Toluene and m- and p-Xylene

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16. ABSTRACT

Fourier transform infrared absorption spectroscopy and differential optical absorption spectroscopy have been used to determine the yields of glyoxal and methylglyoxal from the reaction of hydroxyl radicals with toluene, m-xylene and p-xylene. The yields of glyoxal for the three hydrocarbons ranged from 10 to 20%. The yields of methylglyoxal ranged from 10 to 26%. These yields are too low to be explained by any currently available mechanism of aromatic hydrocarbon oxidation.

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Yields of Glyoxal and Methylglyoxal from the NO_x–Air Photooxidations of Toluene and *m*- and *p*-Xylene

Ernesto C. Tuazon, Roger Atkinson,* Hélène Mac Leod, Heinz W. Biermann, Arthur M. Winer, William P. L. Carter, and James N. Pitts, Jr.

Statewide Air Pollution Research Center, University of California, Riverside, California 92521

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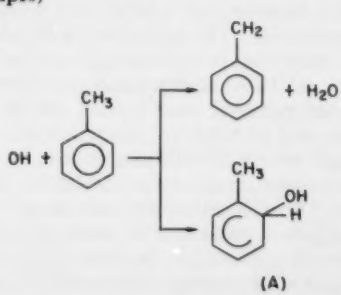
■ The yields of the ring cleavage products glyoxal and methylglyoxal from the reactions of OH radicals with toluene and *m*- and *p*-xylene in the presence of parts per million concentrations of NO have been determined in 1 atm of air at 298 ± 2 K by using in situ long path-length Fourier transform infrared absorption spectroscopy and differential optical absorption spectroscopy. The yields of glyoxal and methylglyoxal derived after correction for their photolysis and reaction with OH radicals were the following respectively: from toluene, 0.111 ± 0.013 and 0.146 ± 0.014; from *m*-xylene, 0.104 ± 0.020 and 0.265 ± 0.035; from *p*-xylene, 0.120 ± 0.020 and 0.111 ± 0.015. These data are important inputs to chemical models of the NO_x–air photooxidations of these aromatic hydrocarbons.

Introduction

Aromatic hydrocarbons are important constituents of gasoline (*1*, *2*) and other commerical fuels (*2*), with gasoline having an aromatic content of ~25–45% (*1*). Black et al. (*1*) have shown that the aromatic content of the total (tailpipe plus evaporative) hydrocarbon emissions is in the range 10–30%. Thus, a complete knowledge of the atmospheric chemistry of the aromatic hydrocarbons is necessary to assess the impacts on photochemical air pollution of their emissions into the atmosphere. However, despite numerous kinetic, product, mechanistic, and computer modeling studies, the reaction pathways involved in the NO_x–air photooxidations of the aromatic hydrocarbons are still incompletely understood (*3*–*6*).

Kinetic and environmental chamber studies have shown that under atmospheric conditions the sole loss process of the aromatic hydrocarbons is due to reaction with the hydroxyl radical (*3*, *6*, *7*). These OH radical reactions have been shown to proceed via two pathways, namely, H atom abstraction from the substituent alkyl groups and OH radical addition to the aromatic ring (*6*–*12*) (taking toluene as an example)



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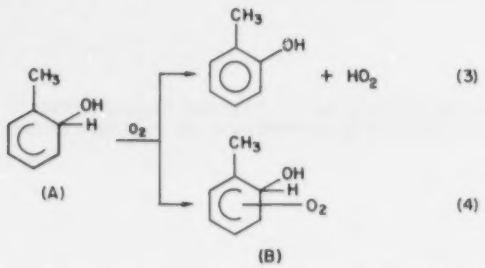
The H atom abstraction route is relatively minor, account for ~8% of the overall reaction for toluene (*12*) and ~2–4% for the xylenes and trimethylbenzenes (*8*, *9*, *11*). While the subsequent chemistry of the benzyl and substituted benzyl radicals appears to be adequately understood (*3*, *6*), the subsequent chemistry of the OH–aromatic adducts is still not well established (*6*). It has been proposed that the OH–aromatic adduct (A) can react with O_2 by two routes (*3*, *4*, *6*):



For toluene the yield of *o*-cresol has been determined to be 13 ± 7% (*12*), and when combined with the *o*-cresol/total cresol formation ratio of ~0.8 (*9*, *13*), this leads to a total isomeric cresol yield of ~16 ± 8%. For the remaining aromatic hydrocarbons the phenolic yields are not presently known.

The pathway involving O_2 addition to the OH–aromatic adducts to form the OH–aromatic–O_2 adducts (B) (reaction 4) and subsequent reactions have been discussed in detail by Atkinson et al. (*3*), Killus and Whitten (*4*), and Atkinson and Lloyd (*6*). Although the reaction sequences proposed are speculative, the α-dicarbonyls glyoxal, methylglyoxal, and biacetyl have been identified and measured from *o*-xylene (*12*, *14–16*) and other aromatic hydrocarbons (*16*). However, only for the formation of biacetyl from *o*-xylene has more than one study been carried out (*12*, *14–16*). In the most recent study, Bandow et al. (*16*) have used long path-length Fourier transform infrared (FT–IR) absorption spectroscopy to determine the yields of the α-dicarbonyls glyoxal, methylglyoxal, and biacetyl from benzene, toluene, the xylenes, and the trimethylbenzenes.

In this work we have used long path-length FT–IR absorption spectroscopy and long path-length differential optical absorption spectroscopy to determine the yields of glyoxal and methylglyoxal from the NO_x–air photooxidations of toluene, *m*-xylene, and *p*-xylene at ~740 torr of air and 298 ± 2 K.

Experimental Section

The NO_x–air photooxidations of toluene, *m*-xylene, and *p*-xylene were carried out in the SAPRC 5800-L evacuable, Teflon-coated environmental chamber, with radiation being provided by a 25-KW xenon arc (*17*). This chamber was equipped with two sets of multiple-reflection White-type optical systems. One set of these multiple-reflection optics, with a base path of 1.30 m, was interfaced to an FT–IR spectrometer. The second set, with a base path of 3.77 m, was interfaced to a differential optical absorption spectrometer (DOAS), as described previously (*18*).

DOAS measurements were carried out by using path lengths from 45.2 to 150.8 m. Glyoxal was monitored in the wavelength region 430–460 nm, as described previously (*18*), with an optimum detection sensitivity of ~3×10^{11} molecule cm^{-3} for the maximum path length used (150.8 m). Methylglyoxal could also be monitored by DOAS in the same wavelength region, but due to its significantly lower differential absorption cross section, the optimum detection sensitivity at the maximum path length used (150.8 m) was ~5×10^{12} molecule cm^{-3}. However, at the shorter path lengths used during the irradiations and in the presence of significant concentrations of NO_2, the unambiguous detection and measurement of methylglyoxal with the DOAS system during these experiments could not be carried out.

Glyoxal, methylglyoxal, and the aromatic hydrocarbons were monitored by FT–IR absorption spectroscopy simultaneously with the DOAS measurements of glyoxal. For the FT–IR measurements, a path length of 62.9 m was routinely used with a spectral resolution (unapodized) of 1 cm^{-1} (optical path difference = 1 cm). Glyoxal and methylglyoxal were monitored at their absorptions at ~2830 cm^{-1}. Analyses of these superimposed bands were carried out by using standard spectra recorded from authentic samples. The first step in these analyses involved the subtraction of the more highly structured band of glyoxal, as verified by the DOAS data (where applicable), followed by the determination of the residual absorption of methylglyoxal. FT–IR detection sensitivities for glyoxal and methylglyoxal were similar, being ~4×10^{12} molecule cm^{-3} at the path length and resolution employed.

Hydroxyl radicals were generated by the photolysis of methyl nitrite in air at wavelengths ≳300 nm (*6*)

$$CH_3ONO + h\nu \rightarrow CH_3O + NO$$

$$CH_3O + O_2 \rightarrow HCHO + HO_2$$

$$HO_2 + NO \rightarrow OH + NO_2$$

NO was included in the reaction mixtures in order to minimize the formation of O_3 and of NO_3 radicals. The initial concentrations of the CH_3ONO–NO–aromatic hydrocarbon–air mixtures were the following: CH_3ONO, ~2.4×10^{14} molecule cm^{-3}; NO, ~1.2×10^{14} molecule cm^{-3}; aromatic hydrocarbon, ~(4–14) × 10^{14} molecule cm^{-3}, with 1 atm (~740 torr) of synthetic air (80% N_2 + 20% O_2) as the diluent gas.

The light intensity in these experiments corresponded to a rate of photolysis of NO_2 in N_2 of 2.22×10^{-3} s^{-1}, and to a biacetyl photolysis rate of (7.47 ± 0.21) × 10^{-5} s^{-1} as determined from an irradiation of a biacetyl–air mixture, with analyses of biacetyl by gas chromatography (*18*).

Results

CH_3ONO–NO–air irradiations of toluene, *m*-xylene, and *p*-xylene were carried out at 298 K and ~740 torr total pressure of air with irradiation times of up to 63 min. The concentrations of the aromatic hydrocarbons, glyoxal, and methylglyoxal were monitored by the FT–IR and/or DOAS technique during these irradiations, and the resulting data are given in Tables I–III of the supplementary material (see paragraph at end of text regarding supplementary material). For toluene and *p*-xylene, the glyoxal concentrations were determined by DOAS, with the methylglyoxal concentrations then being determined by FT–IR spectroscopy (see above). In the case of *m*-xylene both of the individual α-dicarbonyl yields were determined by FT–IR spectroscopy.

The observed α-dicarbonyl yields had to be corrected for reaction with OH radicals and photolysis (*18*) in order to derive the formation yields of these compounds. Since the reaction sequence is

$$\text{OH + aromatic} \xrightarrow{\text{NO, O}_2} Y\ \alpha\text{-dicarbonyl} \qquad (5)$$

$$\text{OH + } \alpha\text{-dicarbonyl} \rightarrow \text{products} \qquad (6)$$

$$\alpha\text{-dicarbonyl} + h\nu \rightarrow \text{products} \qquad (7)$$

Table IV. Glyoxal and Methylglyoxal Yields from the CH_3ONO–NO–Air Photooxidations of Toluene, *m*-Xylene, and *p*-Xylene at Room Temperature and Atmospheric Pressure, Together with the Data of Bandow et al. (*16*)

aromatic hydrocarbon	yield[a] glyoxal: this work	glyoxal: Bandow et al. (*16*)	methylglyoxal: this work	methylglyoxal: Bandow et al. (*16*)
toluene	0.111 ± 0.013	0.15 ± 0.04	0.146 ± 0.014	0.14 ± 0.04
m-xylene	0.104 ± 0.020	0.13 ± 0.03	0.265 ± 0.035	0.42 ± 0.05
p-xylene	0.120 ± 0.020	0.24 ± 0.02	0.111 ± 0.015	0.12 ± 0.02

[a] The indicated errors are two least-squares standard deviations.

where the complex reaction 5 includes reactions 1–4 discussed above and Y is the formation yield of the individual α-dicarbonyls. If the reasonable assumption is made that the OH radical concentrations were essentially constant over the small irradiation periods, then from the measured aromatic hydrocarbon decays

$$[OH] = \frac{1}{k_5(t_2 - t_1)} \ln\left(\frac{[\text{aromatic}]_{t_1}}{[\text{aromatic}]_{t_2}}\right) \quad \text{(I)}$$

where [OH] is the average OH radical concentration over the time period t_1 to t_2, k_5 is the rate constant for reaction 5 (where $k_5 = k_1 + k_2$), and $[\text{aromatic}]_{t_1}$ and $[\text{aromatic}]_{t_2}$ are the aromatic hydrocarbon concentrations at times t_1 and t_2, respectively.

Furthermore

$$[\alpha\text{-dicarbonyl}]_{t_2} = [\alpha\text{-dicarbonyl}]_{t_1}[e^{-(k_6[OH]+k_7)(t_2-t_1)}] + [(Y_{t_1-t_2}[\text{aromatic}]_{t_1}k_5[OH])/[(k_6 - k_5)[OH] + k_7]] \times [e^{-k_5[OH](t_2-t_1)} - e^{-(k_6[OH]+k_7)(t_2-t_1)}] \quad \text{(II)}$$

where $[\alpha\text{-dicarbonyl}]_{t_1}$ and $[\alpha\text{-dicarbonyl}]_{t_2}$ are the α-dicarbonyl concentrations observed at times t_1 and t_2, respectively, and $Y_{t_1-t_2}$ is the derived yield of the individual α-dicarbonyls over the time period t_1 to t_2.

From eq I and II the corrected α-dicarbonyl yields are given by

$$[\alpha\text{-dicarbonyl}]_{t_2}^{cor} = [\alpha\text{-dicarbonyl}]_{t_1}^{cor} + Y_{t_1-t_2}([\text{aromatic}]_{t_2} - [\text{aromatic}]_{t_1}) \quad \text{(III)}$$

where $[\alpha\text{-dicarbonyl}]_{t_1}^{cor}$ and $[\alpha\text{-dicarbonyl}]_{t_2}^{cor}$ are the α-dicarbonyl concentrations at times t_1 and t_2, respectively, after correction for reaction with OH radicals and photolysis.

Rate constants k_5 and k_6 were taken from the literature (*6–8*, *10*, *11*, *18*). Values of k_7 were obtained by ratioing the previously determined photolysis rates for glyoxal, methylglyoxal, biacetyl, and NO_2 (*18*) with the presently determined photolysis rates of NO_2 and biacetyl, yielding values of k_7 for these experimental conditions of 1.66×10^{-5} s^{-1} and 4.0×10^{-5} s^{-1} for glyoxal and methylglyoxal, respectively. Use of these rate data together with eq I–III allowed the observed concentrations of glyoxal and methylglyoxal to be corrected for photolysis and reaction with OH radicals. The correction factors, $[\alpha\text{-dicarbonyl}]_t^{cor}/[\alpha\text{-dicarbonyl}]_t$, were in all cases ≤1.35 for glyoxal and ≤1.51 for methylglyoxal.

The experimental data are given in Tables I–III (see supplementary material) together with the corrected values derived from eq I–III. These corrected α-dicarbonyl concentrations, $[\alpha\text{-dicarbonyl}]_t^{cor}$, are plotted vs. the amounts of aromatic hydrocarbon consumed, $-\Delta[\text{aromatic}]$ [i.e., $([\text{aromatic}]_t - [\text{aromatic}]_{t_0})$] according to eq III in Figure 1, and the yields, Y, of glyoxal and methylglyoxal derived from least-squares analyses of these data are listed in Table IV.

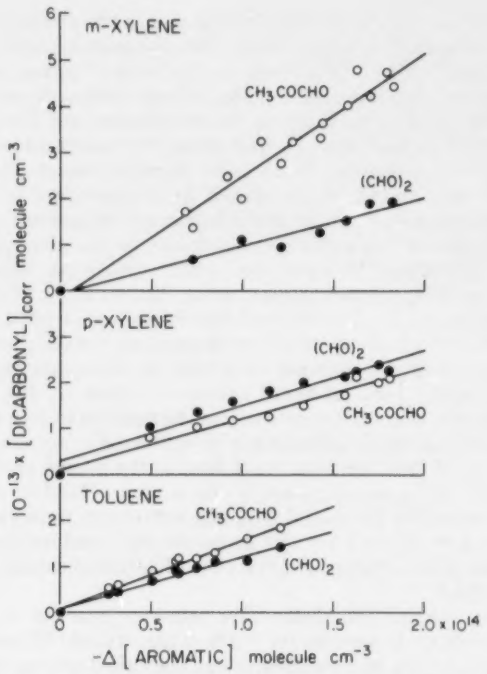
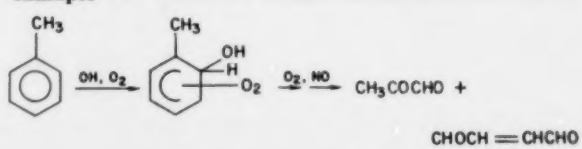


Figure 1. Plot of the glyoxal and methylglyoxal concentrations, corrected for reaction with OH radicals and photolysis (see text), vs. the amount of the aromatic hydrocarbon consumed, for the CH_3ONO–NO–air irradiations of toluene, *m*-xylene, and *p*-xylene.

Discussion

The glyoxal and methylglyoxal yields from toluene, *m*-xylene, and *p*-xylene obtained in this work are compared in Table IV with the yields recently reported by Bandow et al. (*16*). It can be seen that the magnitude of these yields are in good agreement, with the only significant discrepancies being those for the methylglyoxal yield from *m*-xylene and for the glyoxal yield from *p*-xylene, where Bandow et al. (*16*) obtained values higher by factors of ~1.5 and 2.0, respectively, than those of the present work. Clearly, however, the present data and those of Bandow et al. (*16*) define reasonably closely the yields of these α-dicarbonyls from the three aromatic hydrocarbons studied here. Furthermore, the data shown in Figure 1 indicate that within the experimental errors the α-dicarbonyl yields do not increase with the extent of reaction, contrary to expectations based on current chemical mechanisms (*3–5*), which predict that unsaturated 1,4-dicarbonyls are also formed as products. These unsaturated 1,4-dicarbonyls are postulated (*3–6*) to subsequently react to form α-dicarbonyls as secondary products, for example



$$CHOCH{=}CHCHO + OH \xrightarrow{O_2,\ NO} 2(CHO)_2$$

Although these experiments were carried out at concentrations considerably higher than those present in the ambient atmosphere, the observed α-dicarbonyl yields should be applicable to atmospheric conditions. In par-

ticular, in both these experiments and in the atmosphere, the aromatics are consumed solely by reaction with the hydroxyl radical. Moreover, on the basis of current estimates of rate constants for the radical intermediates believed to be formed (*6*), in neither system are the concentrations high enough that these intermediates would react with each other or any other organics present. Hence the α-dicarbonyl yields should be independent of the concentrations of the aromatic hydrocarbons present, over the range of concentrations applicable to the atmosphere and this study. However, the product yields may depend on the NO_x concentrations, since Kenley et al. (*9*) and Hoshino et al. (*13*) observed the formation of nitro aromatics which are expected to depend on the NO_2 levels. These products were not monitored in our experiments, but on the basis of these previous studies (*9*, *13*), the formation of nitro aromatics from the reaction of NO_2 with the OH–aromatic adducts can be estimated to account for $\lesssim$10–15% (and perhaps much less) of the overall product yields. This is confirmed by the study of Bandow et al. (*16*) in which the initial NO_x concentrations were varied from 2×10^{13} to 1.5×10^{14} molecule cm^{-3}, and no dependence of the product yields on the NO_x concentration was reported.

For toluene the abstraction pathway (reaction 1) has been shown to account for $\sim$8% of the overall OH radical reaction (*12*), and reaction 3 has been shown to account for $\sim 16 \pm 8\%$ of the overall reaction (*12*). Hence, the inclusion of reaction pathways resulting in the formation of $\sim$26% of glyoxal and methylglyoxal [together with the corresponding coproducts [*6*)] still account for only $\sim$50% ($\pm$15%) of the overall reaction pathways. Clearly the products and mechanisms of a major portion of the OH–aromatic reactions under these conditions are presently not identified.

The present data thus have major implications for the validity and predictions of present chemical kinetic computer models of aromatic hydrocarbons, since previous chemical computer models (*3*–*5*) have assumed that the reactions subsequent to reaction 4 yield exclusively α-dicarbonyls (together with the corresponding coproducts such as those shown above). These α-dicarbonyl yields are too low to be explained by any of the existing chemical mechanisms, and thus, these present chemical mechanisms (*3*–*5*) are suspect. Obviously, further studies are needed to identify the remaining products and reaction pathways involved under atmospheric conditions following the initial OH radical reaction with the aromatic hydrocarbons.

Acknowledgments

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Supplementary Material Available

Tables I–III listing experimental data for the CH_3ONO–NO–aromatic–air irradiations (3 pages) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper or microfiche (105 × 148 nm, 24× reduction, negatives) may be obtained from Microforms Office, American Chemical Society, 1155 16th St., N.W., Washington, DC 20036. Full bibliographic citation (journal, title of article, author, page number) and prepayment, check or money order for $6.00 for photocopy ($8.00 foreign) or $6.00 for microfiche ($7.00 foreign), are required.

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